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Synthesis of a Low Dielectric Perfluoromethylene Linked Cyanate Resin

by

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Copper coupling of 1,6-diiodoperfluorohexane and para iodoanisole gave 1,6-bis (4'-methoxyphenyl) perfluorohexane in good yield. Demethylation with boron tribromide and subsequent reaction with cyanogen bromide gave 1,6-bis (4'-cyanatophenyl) perfluorohexane. Polymerization of the cyanate with copper acetylacetonate provided a good exotherm for the desired trimerization reaction. Measured dielectric permittivity between 2.3 and 2.4. Discussion of attempted preparation of the free phenol perfluoroalkane linked compounds is presented.

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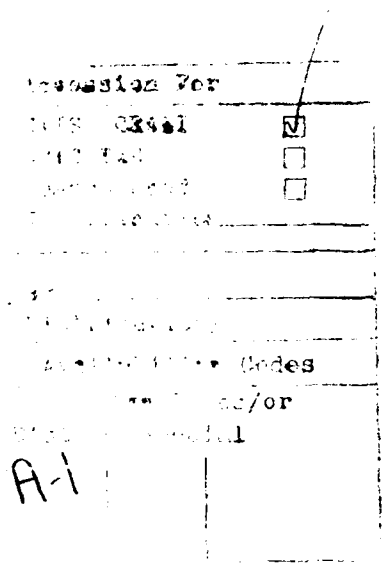

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SYNTHESIS OF A LOW DIELECTRIC PERFLUOROHEXAMETHYLENE LINKED CYANATE RESIN

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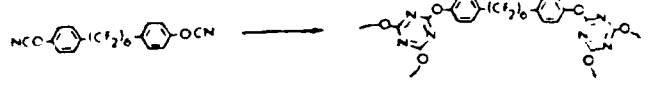
INTRODUCTION

The objective of this work is to synthesize a polymer network wherein the chain structure is polytetrafluoroethylene and the network junction is a triazine linkage. The motivation is to achieve a resin with the dielectric properties of Teflon and the mechanical, thermal and processing properties of a good thermoset. With respect to application as a printed wiring board laminating resin this structure appeared to possess the features of high symmetry, low polar content and low polarizibility proscribed as desirable for low dielectric thermoset resins [1]. Inspection of the above described structure suggests that a nitrile trimerization of an α,ω-perfluoromethylenedinitrile is an obvious synthetic route. However, nitrile trimerization requires severe temperature conditions and is not a high yield reaction. Interestingly, a successful route to this perfluoromethylenetriazine network structure via a perfluoroamidine monomer has been reported 31 years ago [2], but it involved reaction temperatures of 300 to 400°C and condensation of ammonia.

The cyanate trimerization appeared to confer processibility at reasonable cure temperatures with minimal sacrifice of the symmetry and low polarity characteristics of the above mentioned structure. The monomer and polymer we identified for synthesis are depicted in the following polymerization reaction.



In the synthesis and trimerization of cyanates, fluorocarbon chemistry has been found to work a little differently from hydrocarbon chemistry [3]. In this respect, the fluoroalkylphenylcyanate depicted above was similar in reactivity to hydrocarbon phenylcyanates, but different in synthesis due to an instablility of the fluoroalkylphenol. In this paper we present the synthesis and polymerization and characterization of 1,6-bis(4'-cyanatophenyl)dodecafluorohexane (BP12FCY).

EXPERIMENTAL

All reagents and solvents were of reagent-grade quality, purchased commercially and used without further purification unless otherwise noted. Measurements and associated instrumentation are: infrared spectra, Perkin-Elmer Model 1320; ^1H and ^{19}F NMR, Varian Models 360 and 390 using TMS and $CFCl_3$ as internal standards; mass spectra, Varian Saturn Model GC/MS; DSC, DuPont 2100 Thermal Analysis System with a 910 differential scanning calorimeter, permittivity, HP8510 Network Analyzer (0.5-18 GHz). All melting points are uncorrected.

1,6-Bis(4'-methoxyphenyl)dodecafluorohexane(BP12FCMe). A mixture of 18.76 g (80.1 mmol) of 4-iodoanisole, 11.11 g (20.0 mmol) of 1,6-diiododecafluorohexane and 6.35 g (100 mmol) of copper powder in 5 g DMSO was reacted at 125-135°C (24 hr) then 165°C (1.5 hr) followed by sublimation at 110°C/0.025 mmHg. Resublimation gave 8.5 g product as white crystals: mp 77.0-78.5°C; ^1H NMR ($CDCl_3$) 3.80 ppm s (3H), 6.93 ppm d (2H) and 7.50 ppm d (2H); ^{19}F NMR ($CDCl_3$) -107.2 ppm ($ArCF_2$-) and 119.3 ppm (-$(CF_2)_4$-); IR see figure 1.

1,6-Bis(4'-cyanatophenyl)dodecafluorohexane (BP12FCY). By gas tight syringe 1.91 ml (5.04 g, 20.2 mmol) of boron tribromide were added to 40 ml freshly distilled methylene chloride under nitrogen followed by cooling to 0-5°C and dropwise addition of 4.51 g (8.77 mmol) of BP12FOMe dissolved in 100 ml of freshly distilled CH_2Cl_2. After stirring 12 hr at 20°C, the reaction mixture was poured into 150 ml rapidly stirred water, and the organic layer was repeatedly extracted with 200 ml portions water until the water extract was neutral. The CH_2Cl_2 solution was dried over Na_2SO_4, filtered, and IR spectrum of evaporated film checked for methoxy cleavage. To this solution were then added 1.86 g (17.5 mmol) of cyanogen bromide followed by cooling to 5°C (ppt formation at lower temperatures) and dropwise addition of 1.77 g (17.5 mmol) triethylamine dissolved in 6 ml of CH_2Cl_2. The reaction mixture was stirred at 0-5°C for 2.5 hr then allowed to slowly to warm to room temperature with stirring for an additional hour. The reaction mixture was worked up by pouring into 500 ml of stirred water, two extractions with 200 ml of water, Na_2SO_4 drying and evaporation. A tedious recrystalization from cyclohexane yielded 1.70 g (39%) of BP12FCY: mp 75-77°C; ^1H NMR ($CDCl_3$) 3.80 ppm (residual -OCH_3) and 6.8-7.7 ppm (Ar-H); ^{19}F NMR ($CDCl_3$) -158 ppm (4F) and -169 ppm (8F); IR see figure 1; MS no molecular ion, 143 (100%) $CF_2C_6H_4OH$.

BP12FCY Cure. A mixture of 0.990 g BP12FCY and 0.0089 g catalyst solution (0.30 g copper acetylacetonate in 4.00 g nonylphenol [4] was degassed under vacuum (~1 mmHg)/100°C, mixed by stirring after melting and cured at 115°C for 1.5 hr followed by 180°C for 1 hr.

RESULTS AND DISCUSSION

The synthesis of BP12FCY was undertaken by the route depicted in figure 1. The initial plan was to couple p-iodophenol with the diiodoperfluorohexane. However, much difficulty was experienced in isolating a product, and it appears that the p-fluoromethylene substituted phenol is not stable to purification operations. Protecting the phenol with the methoxy group by starting with p-fluoroanisole in place of p-fluorophenol solved this problem, and the bis(methoxyphenyl)perfluorohexane could be separated from the DMSO and purified by sublimation.

The problem now became one of converting the methoxy groups to cyanate groups without having the intermediate phenol undergo decomposition. What was needed is a mild method of cleavage of the anisole and preferably a medium which would allow proceeding immediately to the cyanation reaction without isolating the phenol. Typically, cleavage by hydroiodic or sulfonic acids require temperatures in excess of 100°C [5], however, boron tribromide is reported to effectively demethylate methyl phenyl ethers at or below room temperature in methylene chloride solution [6]. This was particularly attractive because the methylene chloride medium could easily be made neutral and is a good solvent for the low temperature base catalyzed cyanation reaction. An excess of BBr_3 was used, and it appeared from the hydroxyl absorption in the infrared spectrum (figure 2) that a good conversion had been obtained although a residual methoxy is also present.

The cyanation reaction was undertaken after obtaining a neutral aqueous extract and drying the methylene chloride solution. The infrared spectrum (figure 2) indicated that the hydroxyl was quantitatively converted to the cyanate group (2250 cm^{-1}).

Proceeding to the polymerization uncatalyzed cure of the BP12FCY monomer was first attempted. In this instance the DSC thermogram displayed a broad exotherm with a maxima at 297°C which we attributed to the trimerization reaction and a second exotherm onset at ~350°C which we suspect may be associated with decomposition. It has been demonstrated that addition of catalytic quantities of transition metals (copper in particular) in combination with a phenol can markedly lower the

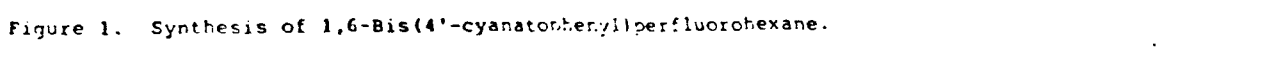


Figure 1. Synthesis of 1,6-Bis(4'-cyanatophenyl)perfluorohexane.

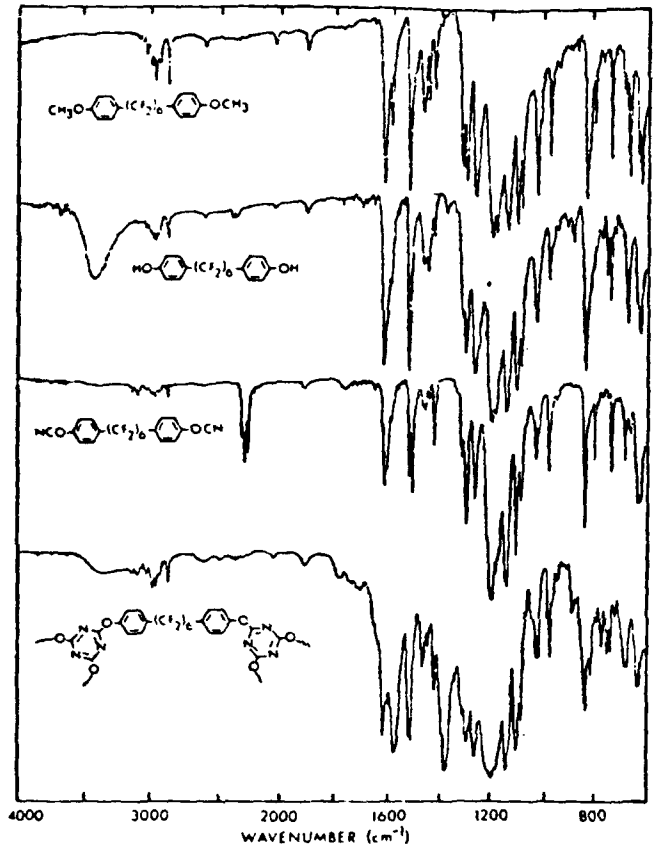


Figure 2. Infrared Spectra of Perfluorohexane-dicyanate, Precursors, Monomer and Resin.

cure temperature and provide much better control over the trimerization exotherm [4]. Addition of 0.89 phr of a copper acetylacetonate/nonylphenol catalyst markedly narrowed and lowered the trimerization exotherm to a 167°C maximum in the DSC thermogram (figure 3). Following a curing schedule of 115°C for 1.5 hr and 180°C for 1 hr, an infrared spectrum indicated the cyanate (2250 cm^{-1}) was completely consumed and a large amount of triazine (1573 and 1375 cm^{-1} [7]) had formed (figure 2).

A measurement of the dielectric permittivity is presented in figure 4. Its response to

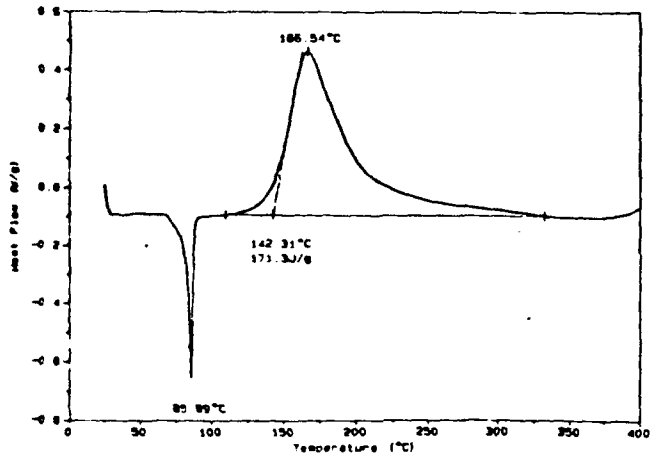


Figure 3. DSC Thermogram of BP12FCY Cure Catalyzed with 0.89 phr CuAcAc/Nonylphenol.

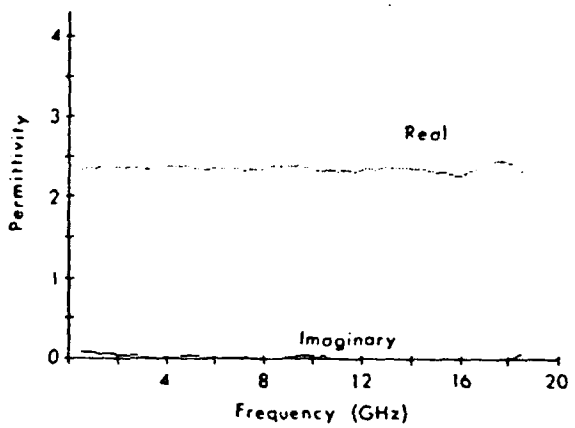
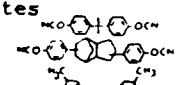
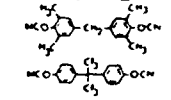
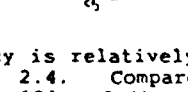
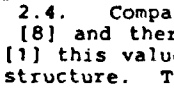


Figure 4. Dielectric Measurement on BP12FCY

Table 1. Dielectric Permittivity of Thermoset and Thermoplastic Resins [1,8].

Resin	Permittivity
FR-4 epoxy	3.6
Polyimide (BMI)	3.2
Polyetherimide	3.1
Polysulfone	3.0
Polycarbonate	3.0
Polybutadiene	2.8
Polyolefin	2.3
Polytetrafluoroethylene	2.0
Cyanates	
	3.1
	2.8
	2.75
	2.66

frequency is relatively flat with a value between 2.3 and 2.4. Compared with other cyanates in specific [8] and thermosets or thermoplastics in general [1] this value appears reasonable for the polymer structure. Table 1 presents permittivity values with various associated resins and structures but has ignored any dependence on frequency. The BP12FCY result presented here is intermediate to the 2.0 for PTFE and the 2.66 for the dicyanate of bisphenol F. The true BP12FCY result may be slightly lower then that reported here since there is a residual quantity of methoxy groups in this synthesis as evidenced by the infrared band at 2845 cm^{-1} in figure 2.

In summary, to lower the dielectric permittivity of a thermoset resin, the approach of connecting perfluoromethylene chains with cyanurate linkages provides a structure that is near equivalent to polyethylene at perfluoromethylene chain length of six. Increased fluoroalkyl content will more closely approach the value of Teflon.

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FINANCIAL STATUS REPORT

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4. Employer Identification Number	5. Recipient Account Number or Identifying Numbe	6. Final Report (X) Yes ( ) No	7. Basis (X) Cash ( ) Accrual
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b. Recipient share of outlays	0.00	0	0
c. Federal share of outlays	0.00	$10,000.00	$10,000.00
d. Total unliquidated obligations			
e. Recipient share of unliquidated obligations			
f. Federal share of unliquidated obligations			
g. Total Federal share (Sum of lines c and f)			
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i. Unobligated balance of Federal funds (Line h minus line g)			

11. Indirect Expense

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b. Rate	c. Base	d. Total Amou	e. Federal Share
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13. Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays unliquidated obligations are for the purposes set forth in the award documents.

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Signature of Authorized Certifying Official	**Date Report Submitted**
Richard L. Anderson	June 1, 1992

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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

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Contract/Grant Title: Synthesis of Derivatives of Alpha Omega Difunctional Perfluoroaliphatic Resins

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a. Number of papers submitted to refereed journals, but not published: 0

b. Number of papers published in refereed journals: 0

c. Number of books or chapters submitted, but not yet published: 0.

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f. Number of patents filed: 0

g. Number of patents granted: 0

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Post-Doctoral Associates: 0
Undergraduate Students: 2
including the number of,
Female Graduate Students: 0
Female Post-Doctoral Associates: 0
Female Undergraduate Student: 1
the number of
Minority Graduate Students: 0
Minority Post-Doctoral Associates: 0
Minority Undergraduate Students: 0
and, the number of
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Asian Post -Doctoral Associates 0
Asian Undergraduate Students: 1

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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

Supplemental page R&T Number: 4132054___01
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Item d:

Printed technical reports & non-refereed papers:

1) A.W. Snow, J.R. Griffith, R.L. Soulen, J.A. Greathouse and J.K. Lodge; Synthesis of a Low Dielectric Perfluoromethylene Linked Cyanate Resin; Proceedings of the ACS Division of Polymeric Materials Sciences and Engineering, San Francisco, 1992

2) Jeffery A. Greathouse; A Method of Synthesizing Perfluoroalkyl-substituted Aromatic Compounds; April 8, 1992, Senior Research, Southwestern University

3) Audrey Lim; A Study of the Water Permeability of Fluoroacrylate Films as Compared to Commercial Films; April 27, 1992, Senior Research, Southwestern University

Item j;

Honors

William Currington Finch Award to Robert L. Soulen, May 9, 1992